EVALUATION AND COMPARISON OF NOVEL, LOW-COST SORBENTS FOR MERCURY CONTROL

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ABSTRACT

The injection of sorbents upstream of a particulate control device is one of the most promising methods for controlling mercury emissions from coal-fired utility boilers with electrostatic precipitators and fabric filters. Studies carried out at the bench-, pilot-, and full-scale have shown that a wide variety of factors may influence the mercury removal effectiveness. These factors include mercury species, flue gas composition, process conditions, existing pollution control equipment design, and sorbent characteristics.

The objective of the program is to obtain the necessary information to assess the viability of lower cost alternatives to commercially available activated carbon for mercury control in coal-fired utilities. Prior to injection testing, a number of sorbents were tested in a slipstream fixed-bed device both in the laboratory and at two field sites. Based upon the performance of the sorbents in a fixed-bed device and the estimated cost of mercury control using each sorbent, seventeen sorbents were chosen for screening in a slipstream injection system at a site burning a bituminous coal/petcoke blend and five were chosen for screening at a site burning PRB coal. Evaluated sorbents were derived from various materials, which include: activated carbon samples from coal, biomass and tires; char sorbents made from coal; flyash derived sorbents; and zeolite-based sorbents.

The economics and performance of the novel sorbents evaluated demonstrate that there are alternatives to the commercial standard. Smaller enterprises may have the opportunity to provide a lower price to their customers under the right set of circumstances.

Introduction

The U.S. Environmental Protection Agency (EPA) has submitted a Mercury Study Report to Congress that states that 52 of the 158 tons of anthropogenic Hg emissions in the United States are from coal-fired utility boilers. On December 14th 2000, EPA announced that it would regulate mercury emissions from coal-fired boilers under Title III of the Clean Air Act Amendments of 1990. EPA plans to issue final regulations by December 15th 2004 and is expected to require compliance by December 2007.

The injection of sorbents upstream of a particulate control device is one of the most promising methods for controlling mercury emissions from coal-fired utility boilers with electrostatic precipitators and fabric filters. Studies carried out at the bench-, pilot-, and full-scale have shown that a wide variety of factors may influence the mercury removal effectiveness. These factors include mercury species, flue gas composition, process conditions, existing pollution control equipment design, and sorbent characteristics.

This program is funded by the Department of Energy's National Energy Technology Laboratory (NETL) to obtain the necessary information to assess the viability of lower cost alternatives to commercially available activated carbon for mercury control in coal-fired utilities. The Electric Power Research Institute (EPRI) is also supporting the program with in kind technical support and in providing test equipment. Prior to injection testing, a number of sorbents were evaluated in a slipstream fixed-bed device both in the laboratory and at two field sites: We Energies' Valley Power Plant (Valley) burning a blend of bituminous coal and petcoke, and Midwest Generation's (Edison International) Powerton Station (Powerton) burning a Powder River Basin (PRB) subbituminous coal. Based upon the performance of the sorbents in the fixed-bed device and the estimated cost of mercury control using each sorbent, seventeen sorbents with projected costs of 25% less than commercially available Norit America's Darco FGD™ carbon, were chosen for screening in a slipstream injection system at Valley and five were chosen for Powerton. The most promising two sorbents were chosen for additional parametric testing through injection into slipstream baghouse and ESP modules.

Experimental

Purpose of Test

The overall goal of this evaluation was to assess the effectiveness of low cost novel sorbents for utilities burning a blend of bituminous coal and petcoke or PRB. Slipstream injection tests were conducted at two coal-fired utilities. Seventeen novel sorbents were evaluated as mercury sorbents at Valley and six sorbents were evaluated at Powerton. Injection testing was conducted using EPRI's multi-Pollution Control Test (PoCT) system configured as a COHPAC baghouse, or a residence-time chamber (which simulates the mercury removal in the first field of an electrostatic precipitator (ESP)). Mercury removal across the slipstream injection device was measured with and without sorbent injection.

Methodology

Evaluating sorbent injection for mercury control began with a series of laboratory and field tests designed to evaluate mercury removal in flue gas specific to the sites tested. To be considered for laboratory evaluation during this program, the sorbent manufacturer was required to provide evidence that the cost for removing mercury (per pound of mercury removed) will be at least 25% less that that of FGD carbon. This cost includes not only the cost for producing the carbon but transportation, handling, feeding, and waste handling costs that may differ from FGD. In addition, sufficient quantities would need to be available to supply at least 100,000 tons per year to the utility market by 2010.

Once cost and availability were determined, the performance potential was characterized. In order to evaluate the potential of any mercury sorbent and model it's performance, the equilibrium adsorption capacity and characteristics of the sorbent must be known. Scientists at URS Group conducted fixed-bed adsorption (breakthrough) tests to generate sorbent equilibrium data for the candidate novel sorbents.

The capacity of the mercury sorbent is determined by exposing a bed of the sorbent for periods, ranging from several minutes to several hours, to simulated flue gas containing mercury and measuring the effluent from the bed until no mercury is removed by the bed (100% breakthrough). The capacity is typically normalized to 50µg/Nm^3 because the capacity of a sorbent is dependent on the concentration of the mercury in the inlet gas stream. For most carbon-based sorbents, the capacity is directly proportional to the inlet mercury level. For example, the capacity at 50µg/Nm^3 is nominally five times that at 10µg/Nm^3. Sorbents are screened by measuring their capacity in the laboratory using simulated low sulfur bituminous or PRB flue gas prior to field-testing in actual flue gas. The purpose of these laboratory tests was to evaluate a number of sorbents at conditions similar to those expected at Valley and Powerton. The test results were used to determine the most appropriate sorbents for the field tests. FGD carbon was used as the benchmark sorbent for this program.

Following laboratory testing, small-scale fixed-bed screening tests on selected sorbents were performed at Valley and Powerton using EPRI's mini sorbent test system. The results of these tests were used to determine which samples to test in a series of small-scale injection tests using EPRI's PoCT system. Some mercury sorbents were later added to the slip-stream screening process without going through the fixed-bed screening because of more recent developments in sorbent technology.

During slipstream injection testing, two particulate-control configurations were tested to project mercury removal using sorbent injection upstream of a COHPAC baghouse and upstream of an ESP. A COHPAC module designed for sorbent injection is also called TOXECON. In the TOXECON configuration three sets of tests were conducted at both Valley and Powerton.

1. Screening. Each available sorbent was injected for about 20 minutes at Powerton and 120 minutes at Valley.

2. Parametric. The two most-promising sorbents from screening and economic criteria considerations were tested at various injection rates and two temperatures with two bag types. Each test condition was held constant for approximately 1.5 hours at Powerton and 4 hours at Valley. FGD was also tested for a benchmark comparison.

3. Long term. The two most-promising sorbents were tested continuously for 8-12 hours at Powerton and 48 hours at Valley. The collected solids from the baghouse hoppers were retained for waste characterization evaluations. FGD was also tested for a benchmark comparison.

In the residence chamber configuration, two selected novel sorbents and FGD were parametrically tested for 20-30 minutes at Powerton and 60-90 minutes at Valley each, with the variables being temperature, injection rate, and residence time.

Plant Description and Test Location

Valley Boiler 3

Tests were conducted at We Energies' Valley Power Plant (Valley), Boiler 3. Valley is a cogeneration facility producing steam for the city of Milwaukee and electricity. The boiler is a Riley Stoker front wall-fired, balanced draft boiler burning a mix of pulverized bituminous coal (85%) and petroleum coke (15%). The boiler is rated at 650,000 pounds of steam per hour. Riley Stoker Model CCV Low NO_x burners are installed in the boiler. Particulate emissions are controlled by an Environmental Elements pulse-jet fabric filter.

Powerton Unit 5

The field testing was conducted at Midwest Generation's Powerton Generating Station, Unit 5. The boiler is a B&W Cyclone boiler burning pulverized subbituminous coal from the Powder River Basin. On both Units 5 and 6, two identical cyclone boilers (nominally 450 MW) are used to power one turbine, rated at 893 MW. Particulate emissions are controlled by a Research Cottrell electrostatic precipitator with a weighted wire design.

Equipment

Fixed-Bed Adsorption Test Equipment

The equilibrium adsorption capacity of each candidate sorbent was evaluated using EPRI supported equipment operated by URS Group. The capacity was determined by mixing the sorbent with quartz sand and packing the mixture in a Teflon™ sorbent reaction column. The sorbent is mixed with sand to reduce the pressure drop through the column and reduce gas tracking through the column. The bed material is supported by a perforated Teflon disk and packed with quartz wool. The column and upstream tubing is temperature controlled and heated to the test temperature for at least 1 hour prior to initiating flow through the column. During testing, a particulate-free gas sample is provided to the reaction column. In the field, an Apogee QSIS™ probe is used to inertially separate and filter the flyash from the gas sample. Approximately 1-2 liters of sample flow is continuously passed through the column. The flue gas flows downward through the column to minimize the chance of selective flow or channeling through the bed. Mercury measurements are made at the inlet and outlet of the

column. The amount of mercury exiting the column is measured on a semi-continuous basis until 100% mercury breakthrough is detected.

Following testing, mercury adsorption breakthrough curves are generated. The percent breakthrough is determined as a function of time by normalizing the measured mercury concentration at the outlet of the sorbent bed to the inlet mercury concentration. The adsorption capacity of the sorbent (µg Hg adsorbed/g sorbent) at any given time "t" is determined by summing the total mass of mercury adsorbed through time "t" (area above the breakthrough curve) and dividing by the sorbent mass. The equilibrium adsorption capacity is defined by the time when the outlet mercury concentration is first equal to the inlet concentration.

Slipstream Injection Equipment

The PoCT system is comprised of several small modules that can be configured in series or interchanged as required by the test matrix. The gas extraction assembly uses a temperature controlled probe, flow meter, flow control valve, and several induced draft fans. The extraction probe is a 0.75 to 1.5-inch diameter stainless steel pipe, depending upon the flowrate for the configuration. The length of the probe is determined following a velocity traverse of the duct so that the gas extraction location is at the duct average gas velocity. After extracting a slipstream of gas from the duct, the gas passes through a QSIS inertial gas separation filter where a particulate-free sample can be obtained for mercury analysis. The gas then flows through the particulate control module(s), another QSIS inertial gas separation filter, through a venturi to measure flow, and an automatic flow control valve. The gas is controlled from 10 to 50 acfm depending on the configuration.

During residence chamber testing, sorbent is injected into an 8-inch diameter tube. The flow through the tube is maintained at nominally 50 acfm. This arrangement minimizes wall-effects caused by the smaller diameter inlet piping and transition zones. A sketch of the residence tube arrangement is shown in Figure 1. Two outlet sample probes were installed in the residence tube to allow measurement at two different residence times.

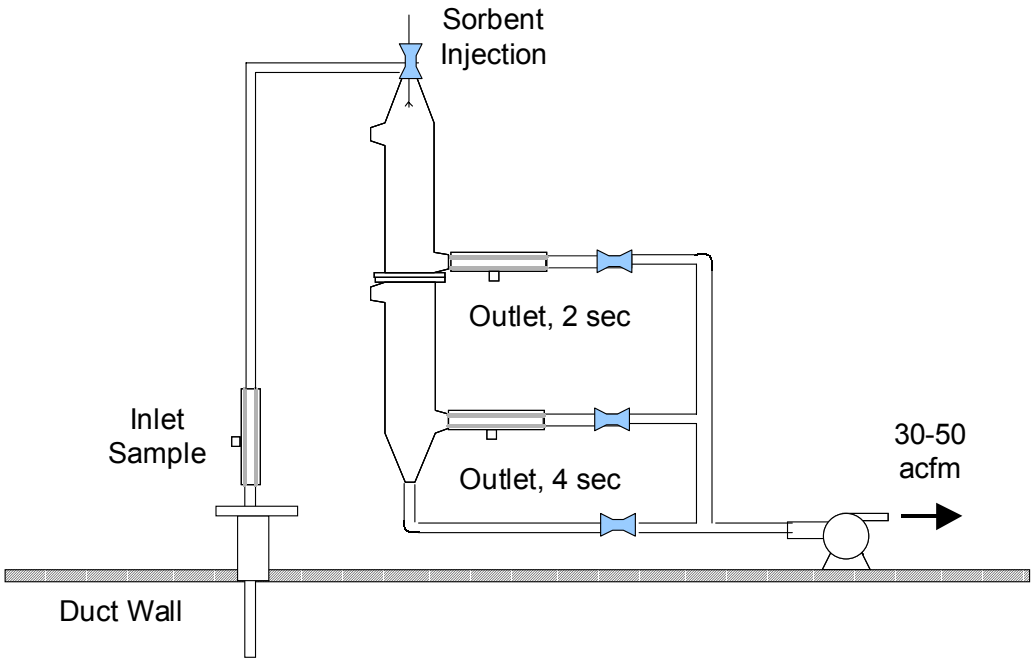


Fig.1. PoCT residence time chamber.

During testing in the TOXECON configuration, two pulse-jet modules were installed in parallel downstream of a tube-wire ESP to assess the differences in sorbent performance with different bag materials. Sorbent was injected upstream of the pulse-jet baghouse module and collected on the bag. The filter bag was 24 inches long and had a flat width of 7.56 inches. Bag cleaning was initiated manually during testing and performed off-line. A sketch of the PoCT TOXECON configuration is shown in Figure 2. As shown, the pulse-jet module is a top-entry design, which minimizes particulate fall-out into the hopper that often is a concern in small-scale systems.

The sorbent injection assembly consists of a small screw feeder and an eductor. Compressed air is used to carry the sorbent from the eductor to the injection port. Several custom-designed helixes were prepared to provide the low injection rates required for this program.

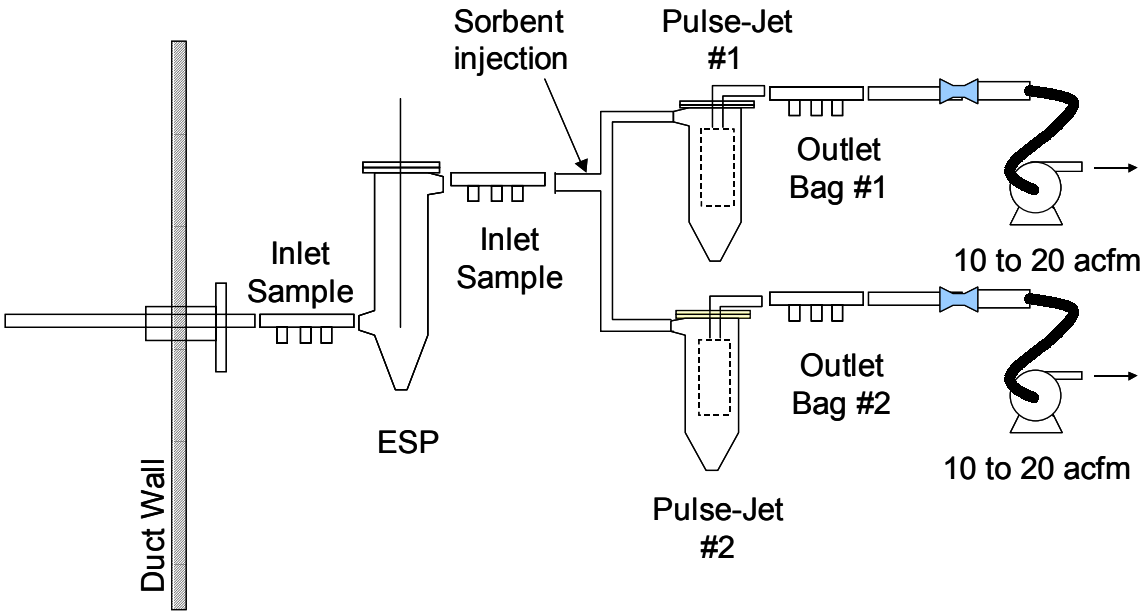


Fig. 2. PoCT configured for TOXECON testing.

Sorbent Descriptions and Selection

Performance evaluations of forty-seven sorbents were conducted in simulated low sulfur eastern bituminous flue gas and twenty-seven in simulated PRB flue gas. These sorbents were identified as potential sorbents for testing based upon economic information provided by the sorbent suppliers and tested during this program, or using existing data from URS Group's testing outside this program. Based upon the results of the laboratory screening tests and estimated sorbent costs, seventeen sorbents were chosen for Valley and eight sorbents chosen for Powerton and characterized in the fixed-bed adsorption test device. Of these, nine sorbents were chosen as low-cost candidates for injection testing at Valley and five sorbents were selected for Powerton. Eight additional sorbents were added to the screening process after the fixed-bed evaluations were completed at Valley either by request of the Program Manager or because suppliers had additional sorbents developed during the projects time frame that meet the original vendor solicitation. The sorbents selected for injection screening are identified in Tables 1 and 2.

Table 1. Descriptions of sorbents evaluated at Valley.

Sorbent	ID	Description
Darco FGD	FGD	Texas lignite coal-based commercial carbon, d50 = 18 μm
Tire Derived Activated Carbon	TDAC	Experimental waste tire-based activated carbon
Corn Char	CFA	Pilot Kiln corn-char; experimental, d50 = 15 μm
Soot	CS80	Experimental carbon from soot, d50 = 6.2 μm
HOK300S	HOK	German lignite coal-based commercial carbon, d50 = 19 μm
STI	STI-020513-B, 020930-C, and A	Separated and treated flyash
Type CB	IAC and IAC 020430-B	Coconut shell-based, iodine impregnated commercial carbon, d50 = 25 μm
Treated Flyash	S-1 and E-1-S	Treated flyash
Activated Carbon	LAC	Lignite activated carbon
Modified Zeolite	PSI-C	Modified zeolite
Activated Carbon	A10 and G	Activated carbon with various treatment applications
Activated Carbon	2002-8680 and 2002-8567	Activated carbon with various treatment applications

Table 2. Descriptions of sorbents evaluated at Powerton.

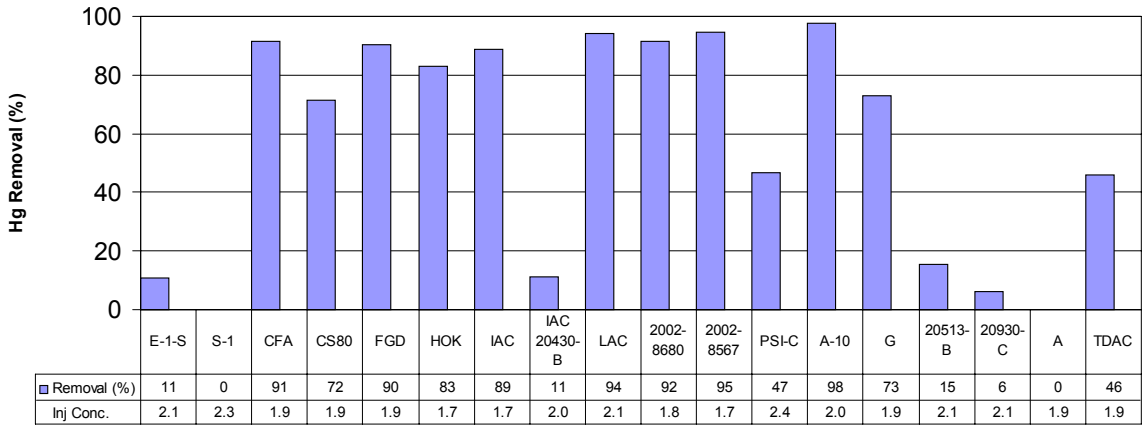
Sorbent	ID	Description
Darco FGD	FGD	Texas lignite coal-based commercial carbon, d50 = 18 μm
Tire Derived Activated Carbon	TDAC	Experimental Waste-tire based activated carbon from
Corn Char	CFA	Pilot Kiln corn-char; experimental, d50 = 15 μm
Soot	CS80	Experimental carbon from soot, d50 = 6.2 μm
HOK300S	HOK	German lignite coal-based commercial carbon, d50 = 19 μm
STI-B	STI-B	Separated and treated flyash

Results and Discussion

COHPAC Baghouse (TOXECON) Configuration

Valley Screening

Sorbent injection screening was conducted at a single injection rate and temperature using the TOXECON-configured PoCT system. During the initial screening period, the sorbents were injected at an injection rate of nominally 2.0 lb/MMacf for 120 minutes to provide a direct comparison of performance. The mercury removal was measured across a Teflon coated woven fiberglass bag. The mercury removal measured during injection of each novel sorbent and FGD is shown in Figure 3. Six of the carbon-based sorbents (FGD, CFA, LAC, 2002-8680, 2002-8567, and A10) demonstrated similar performance (mercury removal due to sorbent injection of greater than 90%). Three of the sorbents (HOK, CS80, and G) removed greater than 70% but less than 90% of the mercury in the flue gas. Six of the sorbents (E-1-S, IAC 020430-B, PSI-C, 020513-B, 020930-C, and TDAC) removed less than 50% of the incoming mercury. Two of the sorbents showed no mercury removal (S1 and A).



	E-1-S	S-1	CFA	CS80	FGD	HOK	IAC	IAC 20430-B	LAC	2002-8680	2002-8567	PSI-C	A-10	G	20513-B	20930-C	A	TDAC
Removal (%)	11	0	91	72	90	83	89	11	94	92	95	47	98	73	15	6	0	46
Inj Conc.	2.1	2.3	1.9	1.9	1.9	1.7	1.7	2.0	2.1	1.8	1.7	2.4	2.0	1.9	2.1	2.1	1.9	1.9

Fig 3. Valley sorbent screening at an injection concentration ~ 2.0 lb/MMacf.

Powerton Screening

During the initial screening period, the sorbents were injected at an injection rate of nominally 1.5 lb/MMacf for 20 minutes to provide a direct comparison of performance. The mercury removal was measured across a Teflon coated woven fiberglass bag. The mercury removal measured during injection of each novel sorbent and FGD is shown in Figure 4.

All carbon-based sorbents demonstrated similar performance except the TDAC. This material agglomerated prior to feeding. Previous samples of this material did not demonstrate these physical properties. It is possible that the lower mercury removal performance is due to the agglomerating nature of this sample.

Following the initial screening tests, the performance of the two most promising sorbents and FGD were characterized by varying the injection concentration and the operating temperature of the TOXECON baghouse. The most promising sorbents were chosen based upon

performance and cost. The two sorbents chosen for additional parametric testing in the TOXECON configuration were the CFA and the HOK.

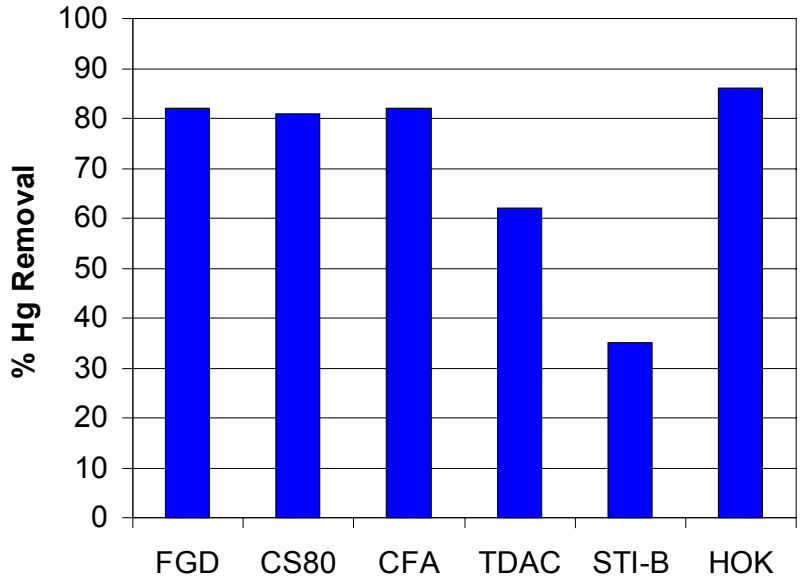


Fig. 4. Powerton sorbent screening at an injection concentration ~ 1.5 lb/MMacf.

Valley Parametric

During parametric testing, the mercury removal across the baghouse was measured at three sorbent injection rates and two operating temperatures. The sorbents (A10, CFA, and FGD) were injected upstream of two baghouse modules, each with a bag of different material. The two modules were configured to operate at the same flow and to clean independently when the pressure drop across the respective bag reached the same set point. The two fabric types were a 2.7-denier PPS (Ryton) felt bag and a 7.0 denier PPS felt Torcon bag.

The effect of temperature on mercury removal was also evaluated during the parametric tests. As shown in Figure 5, the impact of increasing the temperature from 315^{o}F to 350^{o}F slightly increased the mercury removal, except possibly for the FGD at the lowest injection rate, where some degradation is seen. Sorbent A10 showed the largest increase (10% better removal at the higher temperature).

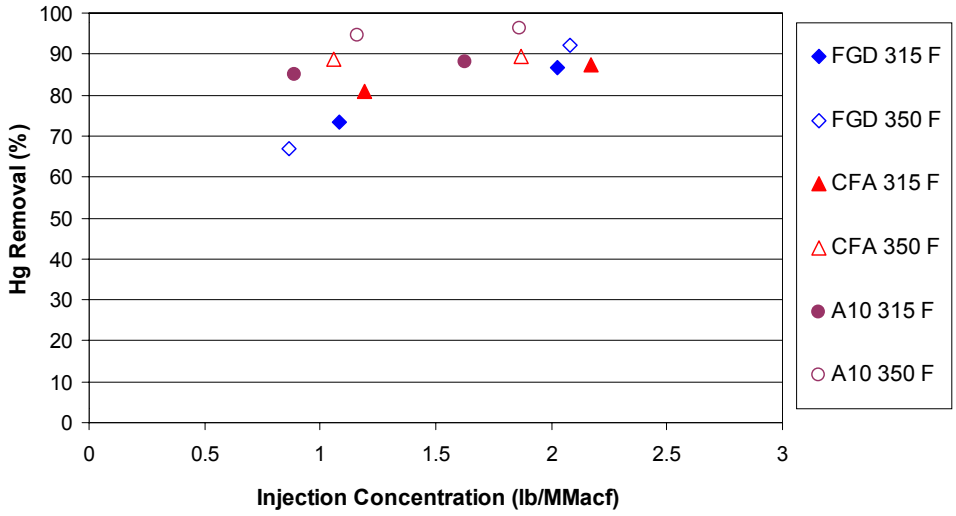


Fig. 5. Valley results from parametric tests.

Following parametric testing, a continuous injection evaluation was conducted for the two most-promising sorbents (CFA and A10) and FGD in the TOXECON configuration. The longer-term injection tests were conducted for 48 hours at a targeted injection rate of 2 lb/MMacf and a temperature of 315ºF. The mercury removal across the bags increased for approximately 2 to 12 hours before leveling off. Both the CFA and A10 reached the percent mercury removal observed in the parametric evaluations within 1 hour of injection for both bag types. The FGD reached similar results but only after 12 hours of injection. The percent mercury removal for all sorbents with the Torcon bag ranged from 93% to 95% and 94% to 99% for the Ryton bag.

Powerton Parametric

The parametric evaluation setup is similar to that of at Valley. The sorbents evaluated were HOK, CFA, and FGD. Two fabric types were used, a Teflon-coated woven fiberglass pulse-jet bag and a 7.0 denier PPS felt Torcon bag.

The effect of temperature on mercury removal was also evaluated during the parametric tests. As shown in Figure 6, the impact of increasing the temperature from 300^{o}F to 350^{o}F is insignificant, except possibly for the CFA at the lowest injection rate, where some degradation is seen.

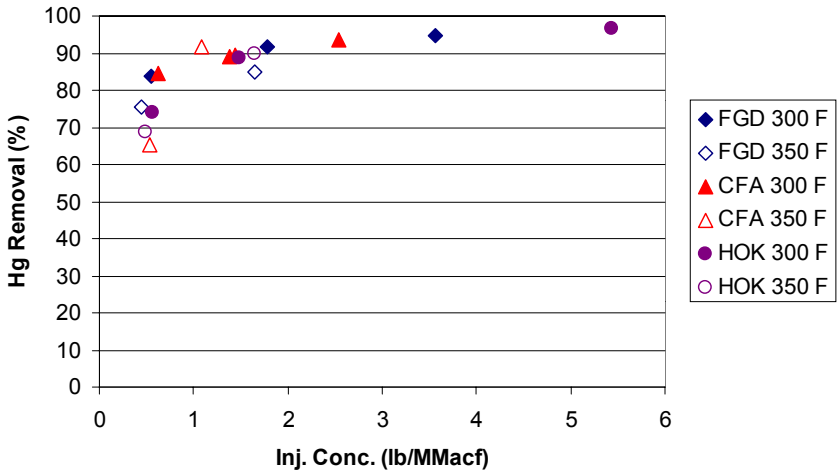


Fig.6. Powerton results from parametric tests.

Following parametric testing, a continuous injection (2.0 lb/MMacf) test was conducted for two sorbents, HOK and CFA, and FGD in the TOXECON configuration. The longer-term injection test was conducted for 8 to 12 hours. The mercury removal across the bags increased for approximately 2 hours before leveling off. The mercury removals were greater than 80% for all sorbents.

Residence Chamber Configuration

Valley

Similar to the TOXECON tests, the mercury removal across the residence chamber was measured at three sorbent injection rates at an operating temperature of 315ºF and at one injection rate at a temperature of 350ºF for two different residence times. The residence times corresponded to nominally 2 and 4 seconds. The 4-second sample appears to correlate fairly well with the mercury removal measured across the first field of an ESP for the limited data set available. The maximum reasonable injection concentration identified for these tests is 15 lb/MMacf based upon cost projections for FGD.

The two novel sorbents identified for parametric testing in the residence chamber were the CFA and CS80. The mercury removal increased with residence time for all sorbents tested but one (CFA at 8 lb/MMacf). The largest improvement from 2 to 4 seconds was with the CS80 sorbent at an injection rate of 8 lb/MMacf. All sorbents demonstrated less than 70% mercury removal for the range of sorbent injection concentrations tested (2.5 to 15 lb/MMacf). Of these three sorbents, it appears that the CS80 demonstrated the higher mercury removal, which may be a result of the significantly smaller particle size (d50 = 6.2 µm compared to 15 and 18 µm for the CFA and FGD, respectively).

The three untreated sorbents were evaluated at 315°F and 350°F at a target injection concentration of 8 lb/MMacf to determine the effect of temperature on mercury removal effectiveness. There was little effect on performance for the FGD and the CFA materials. The performance did degrade for the CS80 material at the higher temperature.

Powerton
The three novel sorbents identified for parametric testing in the residence chamber were the CFA, IAC, and CS80. The mercury removal at 300ºF increased with residence time for all sorbents tested. The largest improvement from 2 to 4 seconds was with the IAC sample. Except for IAC, all samples demonstrated less than 50% mercury removal for the range of sorbent injection concentrations tested (2.5 to 15 lb/MMacf). Of these three sorbents, it appears that the CS80 demonstrated the higher mercury removal, which may be a result of the significantly smaller particle size (d50 = 6.2 µm compared to 15 and 18 µm for the CFA and FGD respectively). The IAC sample demonstrated much higher mercury removal than any of the untreated carbon samples. Untreated activated carbons are often not effective removing mercury from ambient air and carbons treated with a halogen species such iodine or chlorine or sulfur treated carbons are used. It is possible that in flue gas produced from burning low chlorine coals, such as most PRB coals, the HCl present in the flue gas is not adequate to "in situ treat" the sorbents at the high sorbent injection rates required for mercury removal in an ESP

The three untreated sorbents were evaluated at 300^{o}F and 350^{o}F at a target injection concentration to determine the effect of temperature on mercury removal effectiveness. There was little effect on performance for the FGD and the CFA materials. The performance did degrade for the CS80 material at the higher temperature.

Conclusions

Seventeen sorbents were evaluated at Valley and five at Powerton, plus a baseline sorbent (FGD), to assess the effectiveness of low cost sorbents injected for mercury control at plants burning either a bituminous coal and petcoke blend or PRB coal. At both utilities, selected low-cost novel sorbents for mercury control either were comparable or exceeded that of the commercial sorbent standard. Mercury removals of greater than 90% were achieved in the EPRI's PoCT system. There are many factors that can affect mercury removal at coal-fired utilities including mercury species, flue gas composition, process conditions, existing pollution control equipment design, and sorbent characteristics. Not all novel sorbents will perform universally. Analysis of the flyash taken from the pilot-scale system will yield waste characterization results for the TOXECON long-term tests. This will help in deciding the economic impacts of fly-ash utilization. The economics and performance of the novel sorbents evaluated demonstrate that there are alternatives to the commercial standard. Smaller enterprises may have the opportunity to provide a lower price to their customers under the right set of circumstances.

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